

Loss of PM_{2.5} Nitrate from Filter Samples in Central California

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ABSTRACT

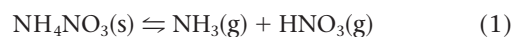
Evaporative loss of particulate matter (with aerodynamic diameter $<2.5\ \mu\text{m}$, [PM_{2.5}]) ammonium nitrate from quartz-fiber filters during aerosol sampling was evaluated from December 3, 1999, through February 3, 2001, at two urban (Fresno and Bakersfield) and three nonurban (Bethel Island, Sierra Nevada Foothills, and Angiola) sites in central California. Compared with total particulate nitrate, evaporative nitrate losses ranged from $<10\%$ during cold months to $>80\%$ during warm months. In agreement with theory, evaporative loss from quartz-fiber filters in nitric acid denuded samplers is controlled by the ambient nitric acid-to-particulate nitrate ratio, which is determined mainly by ambient temperature. Accurate estimation of nitrate volatilization requires a detailed thermodynamic model and comprehensive chemical measurements. For the 14-month average of PM_{2.5} acquired on Teflon-membrane filters, measured PM_{2.5} mass was 8–16% lower than actual PM_{2.5} mass owing to nitrate volatilization. For 24-hr samples, measured PM_{2.5} was as much as 32–44% lower than actual PM_{2.5} at three California Central Valley locations.

INTRODUCTION

The U.S. Environmental Protection Agency (EPA) has established National Ambient Air Quality Standards for PM_{2.5} (particles with aerodynamic diameter $<2.5\ \mu\text{m}$) and has published a Federal Reference Method (FRM) for measuring it that entails collecting PM_{2.5} on a

Teflon-membrane filter and determining its mass gravimetrically.¹ Some PM_{2.5} components, such as ammonium nitrate (NH₄NO₃), are volatile and can leave the filter before gravimetric analysis. NH₄NO₃ is a major component of PM_{2.5} and PM₁₀ (particles with aerodynamic diameters $<10\ \mu\text{m}$) in California's Central Valley.

Ambient particulate NH₄NO₃ is formed by a reversible reaction between gaseous ammonia (NH₃) and nitric acid (HNO₃). At equilibrium:



Stelson and Seinfeld² described the dependence of this equilibrium on temperature and relative humidity (RH). Dissociation of NH₄NO₃ increases with increasing temperature and remains constant for a given temperature below the deliquescence RH, which is 62% at 25 °C.³ Above the deliquescence RH, dissociation decreases rapidly with increasing RH.

It has long been recognized that NH₄NO₃ is lost through evaporation from filters during sampling.^{4–8} This has important implications for accurate assessment of PM_{2.5} under federal and state regulations. During the California Regional PM₁₀/PM_{2.5} Air Quality Study (CRPAQS) and Fresno Supersite operations from December 1999 through January 2001, nitrate (NO₃[–]) concentrations ranged from 0 to 60 $\mu\text{g}/\text{m}^3$, constituting as much as 54% of PM_{2.5} mass. The highest NO₃[–] concentration was found in winter. Chow et al.⁹ reported elevated wintertime PM_{2.5} and PM₁₀ NO₃[–] concentrations in the San Joaquin Valley (SJV) during the Valley Air Quality Study in 1988–1989. NO₃[–] episodes were regional, with corresponding peak concentrations at urban and nonurban sites. NH₄NO₃ was also a major component of PM_{2.5} during the 1995 Integrated Monitoring Study at two urban (Fresno and Bakersfield) and two nonurban (Chowchilla and Kern Wildlife Refuge) sites in the SJV.¹⁰

Zhang and McMurry¹¹ presented theoretical relationships describing evaporative loss of volatile compounds 1159 such as NH₄NO₃ from filter-substrate and impactor

IMPLICATIONS

Evaporative loss of ammonium nitrate negatively biases PM_{2.5} mass in areas like central California, where nitrate is high. This bias cannot be accurately estimated even with complex thermodynamic equilibrium modeling based on comprehensive gas-phase and particulate measurements. The most straightforward means of accounting for ammonium nitrate volatilization is to measure it directly using a gas-denuded sampler containing a nitric acid-absorbent backup filter.

samplers. The degree of volatilization depended mainly on the relative abundances of ambient gaseous HNO_3 and particulate NO_3^- , the amount of gas denuded during sampling, and on the pressure drop through the sampler. Cheng and Tsai¹² conducted laboratory experiments with monodisperse NH_4NO_3 particles and found that evaporative losses decreased as the thickness of the particle "cake" on the filter increased. Losses were higher at low particle concentrations. Chang et al.¹³ tested a particle preconcentrator for use in cascade impactor and filter samplers. Reducing the gas-to-particle ratio by preconcentrating the particles reduced NH_4NO_3 evaporation in both types of samplers.

Hering and Cass¹⁴ assessed the impact of NO_3^- volatilization on $\text{PM}_{2.5}$ mass acquired from Teflon-membrane filters during the 1986 Caltech study and the 1987 Southern California Air Quality Study in the South Coast Air Basin. They found that NO_3^- volatilization was greatest during the warm months and during the warmest periods of the day. Volatilized NH_4NO_3 was up to 60% of measured $\text{PM}_{2.5}$ mass. Volatilization was driven by depletion of the gas phase (i.e., denuding of NH_3 or HNO_3 before the particle filter) and by an increase in the temperature of the filter substrate relative to the ambient temperature. John et al.¹⁵ demonstrated that anodized aluminum inlets on dichotomous samplers effectively remove gaseous HNO_3 .

Ashbaugh and Eldred⁸ examined data from the California Acid Deposition Monitoring Program (CADMP) from 1988 to 1994. The CADMP sampler collects total particulate NO_3^- on a nylon-membrane filter preceded by a HNO_3 denuder and collects particulate NO_3^- on a parallel Teflon-membrane filter in an undenuded channel. They conducted an experiment during winter 1997 in Bakersfield, CA, using an Interagency Monitoring of Protected Visual Environments (IMPROVE) sampler with a configuration similar to the CADMP sampler. The face velocities of the CADMP and IMPROVE samplers were 23.8 and 100 cm/sec, respectively. In general, both samplers lost similar amounts of NO_3^- . Although the CADMP and IMPROVE samplers were not collocated, Ashbaugh and Eldred⁸ concluded that differences in face velocity did not affect NH_4NO_3 volatilization.

In this article, the spatial and temporal variations of $\text{PM}_{2.5}$ NH_4NO_3 volatilization in the SJV during CRPAQS are examined. The factors responsible for this sampling artifact are evaluated and reconciled with theory. Additional measurements at the Fresno Supersite during and after the CRPAQS are used to facilitate this analysis.

EXPERIMENTAL WORK

Aerosol sampling was conducted at two urban (Fresno and Bakersfield) and three nonurban (Bethel Island, Sierra

Nevada Foothills, and Angiola) anchor sites (Figure 1). DRI (Reno, NV) sequential filter samplers (SFS) were operated at all five sites. An Andersen Instruments (Smyrna, GA) multiple channel reference ambient air sampler (RAAS, a speciation sampler) and two Andersen Instruments single-channel FRM samplers, equipped with Teflon-membrane (Pall Sciences, R2PJ047, Ann Arbor, MI) and quartz-fiber (Pall Sciences, QAT2500-VP, Ann Arbor, MI) filters, were operated at the Fresno Supersite.¹⁶ All of the samplers were preceded by $\text{PM}_{2.5}$ size-selective inlets: Sensidyne Bendix 240 cyclone for the SFS; AIHL cyclone for the RAAS; and EPA WINS impactor for the FRM.¹⁷ The SFS and RAAS samplers were preceded by aluminum oxide tubular and sodium carbonate-coated glass annular denuders, respectively, to remove gaseous HNO_3 . Experiments with the CADMP sampler, which is similar to the SFS sampler, showed that the efficiency of the aluminum oxide denuder exceeded 90% for HNO_3 .¹⁸ Similar efficiencies were reported for a sodium carbonate honeycomb denuder with respect to HNO_3 and HONO .¹⁹ The RAAS sampler also contained an undenuded channel in which NO_3^- was collected on a quartz-fiber filter.

Sampler configurations are shown in Figure 2. Non-volatilized NO_3^- was collected on 47-mm front quartz-fiber filters in the SFS, RAAS, and FRM samplers. Volatilized NO_3^- was collected in HNO_3 -denuded channels on back-up sodium chloride impregnated cellulose-fiber filters (31ET, Whatman, Hillsboro, OR) and back-up nylon-membrane (Nylasorb, Pall Sciences, Ann Arbor, MI) in the SFS and RAAS samplers, respectively. NO_3^- was analyzed on distilled-deionized water extractions of the filters by ion chromatography.²⁰ A citric acid impregnated cellulose-fiber filter following the Teflon-membrane filter in the SFS

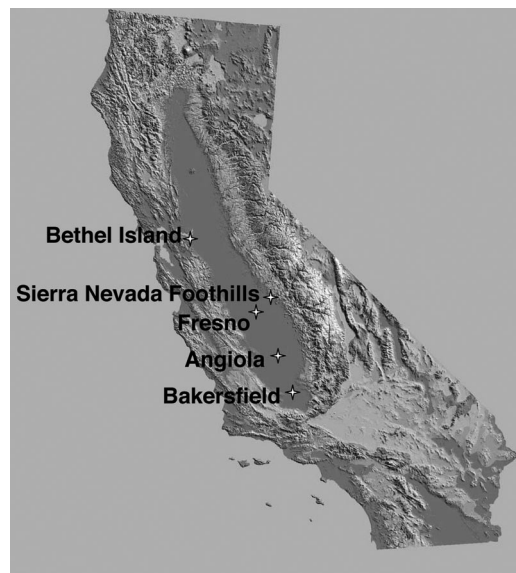
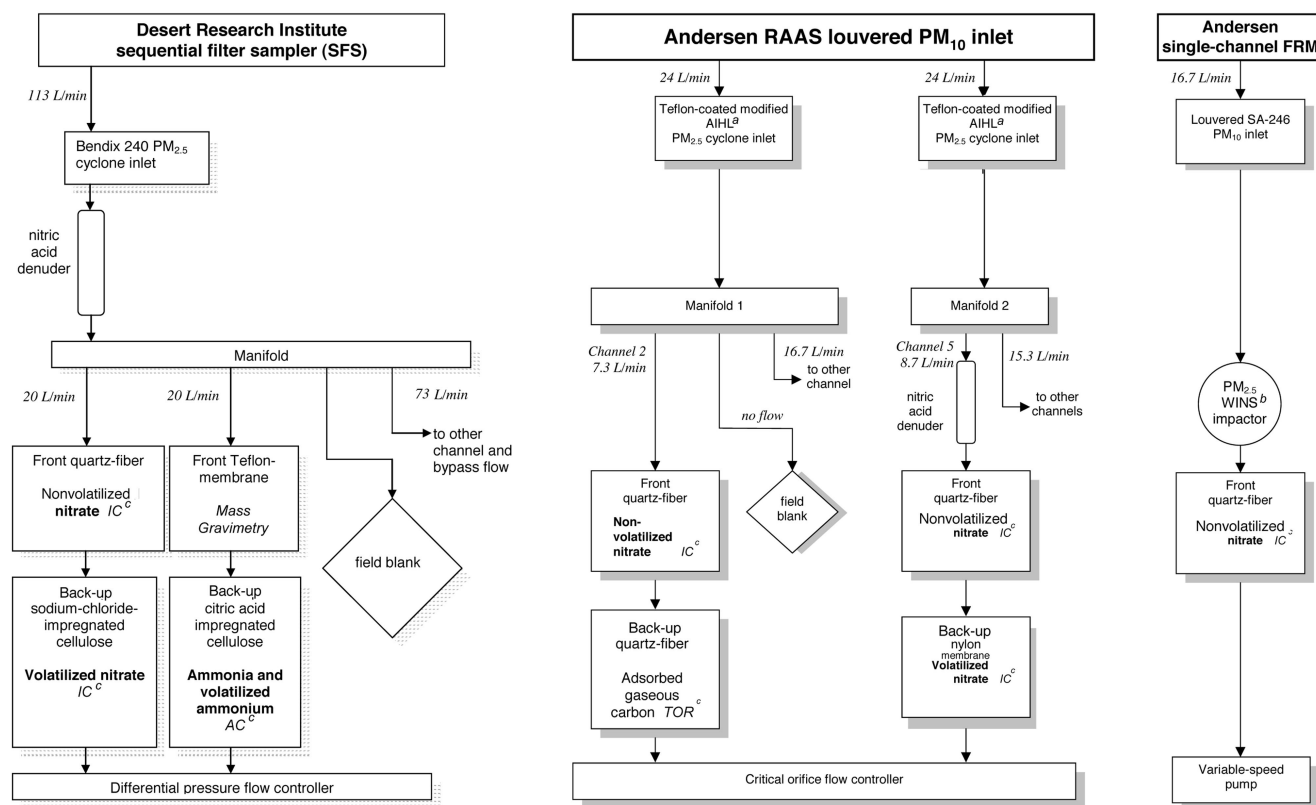


Figure 1. Locations of CRPAQS anchor sites.



^a Air and Industrial Hygiene Laboratory

^b Well Impactor Ninety Six

^c IC: Ion Chromatography; AC: Automated Colorimetry; TOR: Thermal/Optical Reflectance

Figure 2. Sampling configurations for DRI SFS, Andersen RAAS, and Andersen FRM.

captured ambient NH_3 and particulate ammonium (NH_4^+) volatilized to NH_3 from the Teflon-membrane filter. The sum of the SFS quartz-fiber filter NH_4^+ (adjusted to equivalent NH_3) and citric acid impregnated filter NH_3 provides the "total equivalent NH_3 " (particle plus gas).

Twenty-four-hour samples were collected on the EPA every-sixth-day schedule starting on December 2, 1999, at the Fresno, Angiola, and Bakersfield sites and on December 2, 2000, at the Bethel Island and Sierra Nevada Foothills sites, and ending on February 3, 2001. Daily SFS samples were collected at Fresno and Angiola during a 2000 fall intensive study on the following dates: October 14, October 16–20, October 22–24, and November 2–9. A winter intensive study was conducted at all five anchor sites from December 15 to 18 and December 26 to 28, 2000, and from January 4 to 7 and January 31 to February 3, 2001, when SFS samples were collected from 12:00 a.m. to 5:00 a.m., 5:00 a.m. to 10:00 a.m., 10:00 a.m. to 1:00 p.m., 1:00 p.m. to 4:00 p.m., and 4:00 p.m. to 12:00 a.m. PST. HNO_3 and NH_3 were also determined on the same schedule using DRI sequential gas samplers.²¹ Total NO_3^- ($\text{TNO}_3^- = \text{gaseous } \text{HNO}_3 \text{ [as equivalent } \text{NO}_3^-] \text{ plus nonvolatilized and volatilized } \text{NO}_3^-$) in the sequential gas

samplers was collected on sodium chloride impregnated cellulose-fiber filters in an undenuded sampling stream. Particulate NO_3^- was collected on the same filters in a parallel HNO_3 -denuded channel, and HNO_3 was determined by the difference between the undenuded and denuded NO_3^- concentrations (i.e., by denuder difference). NH_3 was also determined by denuder difference using citric acid impregnated cellulose-fiber filters and citric acid coated denuder. Hourly HNO_3 was measured continuously at the Fresno Supersite using a TEI-42C chemiluminescence analyzer (Thermal Electron Corp., Franklin, MA) with undenuded and HNO_3 -denuded channels.¹⁶ Meteorological measurements of temperature and RH were available for the Fresno and Bakersfield sites.

RESULTS AND DISCUSSION

Figure 3 shows a linear, inverse relationship between 24-hr average temperature and RH at the Fresno and Bakersfield sites. Trends were similar at both sites. Given the dependence of the NH_4NO_3 equilibrium on temperature and RH, this variation should control the distribution of gaseous and particulate NO_3^- and influence NH_4NO_3 sampling artifacts in the SJV.

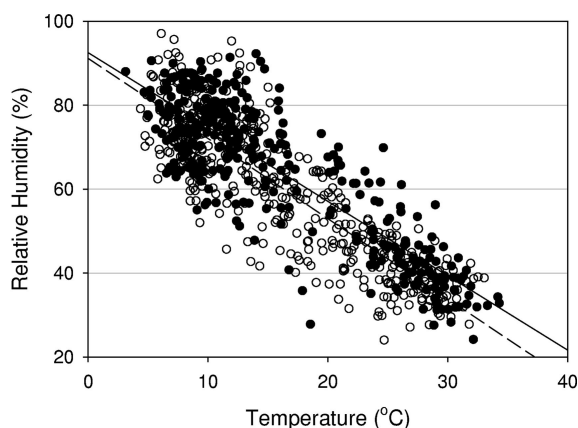


Figure 3. Twenty-four-hour average temperature ($^{\circ}\text{C}$) and (relative humidity %) at the Fresno and Bakersfield sites between December 2, 1999, and February 3, 2001.

Seasonal averages of nonvolatilized and volatilized NO_3^- from 24-hr average SFS samples at the Fresno, Angiola, and Bakersfield sites are shown in Figure 4. The highest and lowest total particulate NO_3^- (PNO_3^- , the sum of nonvolatilized and volatilized NO_3^-) occurred

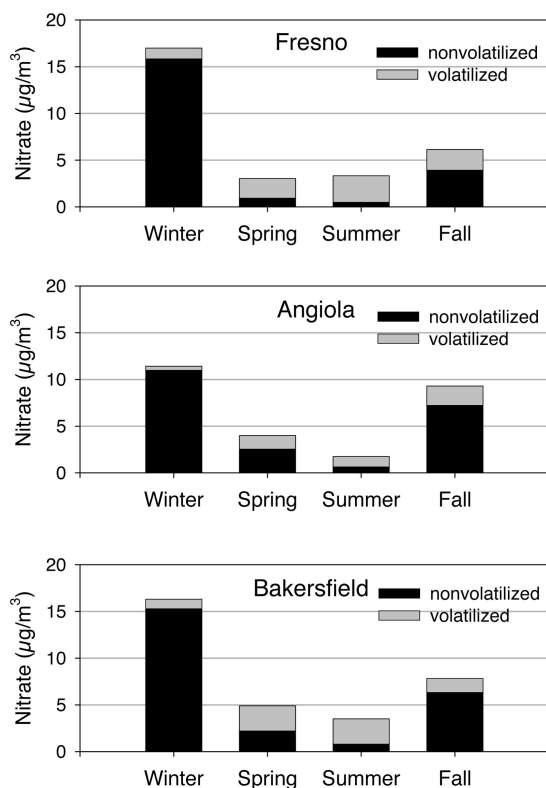


Figure 4. Seasonal average of nonvolatilized and volatilized NO_3^- concentrations measured with front quartz-fiber filters and back-up sodium chloride impregnated cellulose-fiber filters, respectively, at the Fresno, Angiola, and Bakersfield sites in California using HNO_3 -denuded SFS for samples acquired from December 2, 1999, to December 2, 2000, with every-sixth-day EPA sampling schedules: winter, December to February; spring, March to May; summer, June to August; fall, September to November.

during winter and summer, respectively, at the Bakersfield and Angiola sites. The lowest concentrations were similar during spring and summer at Fresno. Seasonal average volatilized NO_3^- in PNO_3^- ranged from 3.5% at Angiola during winter to 84% at Fresno during summer. These results are consistent with those observed by Shaw et al.,⁵ Hering and Cass,¹⁴ and Ashbaugh and Eldred.⁸ Monthly average ratios of volatilized NO_3^- : PNO_3^- at the Fresno, Angiola, and Bakersfield sites, along with average temperature at Fresno and Bakersfield, are plotted in Figure 5. Monthly volatilized NO_3^- is low during winter and reached 60–80% in summer. As shown in Table 1, monthly average volatilized NO_3^- as a percentage of PNO_3^- was highly correlated among sites and also with Fresno monthly average temperature. Monthly average temperature at Fresno and Bakersfield was also highly correlated.

Figure 6 examines daily average fraction of volatilized NO_3^- at the Fresno and Angiola sites along with daily average temperature at Fresno during the 2000 fall intensive period. The fraction of volatilized NO_3^- decreased substantially at both sites, whereas temperature at Fresno decreased by $\sim 10^{\circ}\text{C}$ over the intensive period. Figure 7 shows period-average temperature at Fresno and Bakersfield and the fraction of volatilized NO_3^- at those sites during the 2000–2001 winter intensive period. Again, the fraction of volatilized NO_3^- at the Fresno and Bakersfield sites was correlated with temperature and the fraction peaked during the afternoon sampling period (1:00 p.m. to 4:00 p.m. PST). This corresponded to an increase in temperature of 5–6 $^{\circ}\text{C}$ from the previous period at both sites.

Figure 8 compares daily nonvolatilized NO_3^- from the front quartz-fiber filters in the denuded and undenuded channels of the RAAS sampler (Figure 2) in Fresno

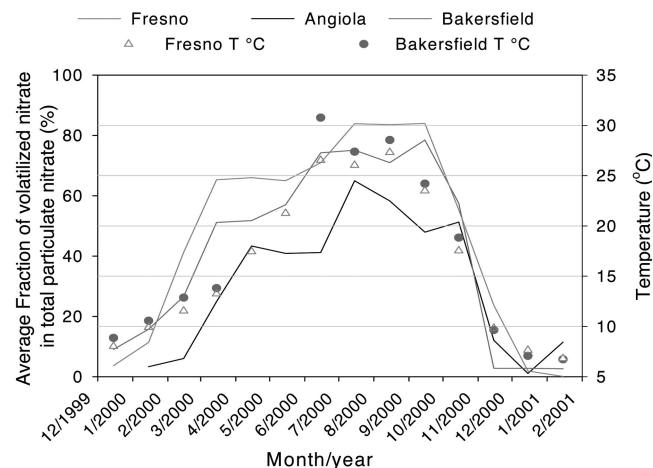


Figure 5. Monthly average ratio (%) of volatilized NO_3^- to total PNO_3^- (which is the sum of nonvolatilized and volatilized NO_3^-) from HNO_3 -denuded SFS along with monthly average temperature ($^{\circ}\text{C}$) at the Fresno and Bakersfield sites in California.

Table 1. Intersite correlations between monthly average ratios of volatilized NO_3^- to total PNO_3^- (which is the sum of nonvolatilized and volatilized NO_3^- in HNO_3 -denuded channel) at the Fresno, Angiola, and Bakersfield sites and monthly average temperature (T in $^\circ\text{C}$) at Fresno.

	Fresno Ratio	Angiola Ratio	Bakersfield Ratio	Fresno T
—	1	—	—	—
Angiola ratio	0.88	1	Fresno	—
Bakersfield ratio	0.91	—	1	—
Fresno T	0.91	0.92	0.95	1

for warm (May–September) and cold (November–March) months over several years. The largest difference is seen during the warmer months when the average ratio of denuded-to-undenuded NO_3^- was 0.41 ± 0.21 . These ratios were much higher (1.08 ± 0.34) during the colder months.

Consistency with Theory

According to Zhang and McMurry,¹¹ the sampling efficiency (η_e) for particulate NH_4NO_3 at equilibrium with gaseous NH_3 and HNO_3 at the sampler inlet (saturation ratio [SR] = 1) is:

$$\eta_e = \{1 + (\Delta P/[P_o - \Delta P]) \rho_e/C_m\}^{-1} \quad (2)$$

where P_o and ΔP are the ambient atmospheric pressure and pressure drop across the filter, respectively; ρ_e is the ambient HNO_3 concentration over the sampling period; and C_m is the particulate NO_3^- concentration measured on an unreactive filter. The SR is the actual partial pressure of the gas above the filter divided by its partial pressure at equilibrium.

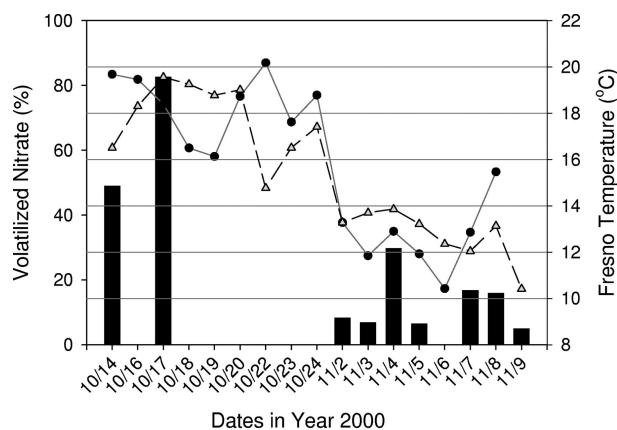


Figure 6. Daily ratio (%) of volatilized NO_3^- to total PNO_3^- at the Fresno (solid circle) and Angiola (solid bar) sites, along with temperature ($^\circ\text{C}$; triangle) at Fresno during the 2000 fall intensive study.

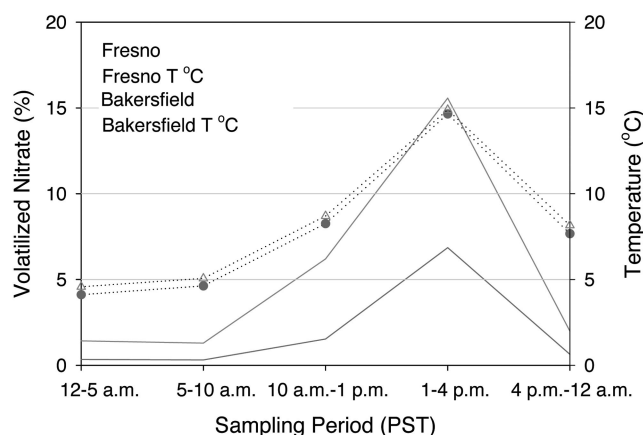


Figure 7. Average diurnal variation of the ratio (%) of volatilized NO_3^- to total PNO_3^- (which is the sum of nonvolatilized and volatilized NO_3^-), along with temperature ($^\circ\text{C}$) at Fresno and Bakersfield during the 2000–2001 winter intensive study.

When both NH_3 and HNO_3 have been removed (e.g., by denuders) at the sampler inlet (SR = 0), the η_e is:

$$\eta_e = \{1 + (P_o/[P_o - \Delta P]) \rho_e/C_m\}^{-1} \quad (3)$$

Corresponding RAAS filter samples (every-sixth-day schedule) and continuous HNO_3 concentrations in Fresno are available from December 2000 through April 2002. Figure 9 compares daily and monthly average NO_3^- evaporative losses with those expected from theory. Because NH_3 was not removed in the RAAS NO_3^- sampling channel, the effective SR should lie between 0 and 1. A laboratory experiment showed that the pressure drop across a quartz-fiber filter at the flow rate of 20 L/min was 2.7%. Theoretical sampling efficiencies for SR = 0 and SR = 1, calculated according to eq 3 and eq 2, respectively, and assuming a pressure drop of 2.7%, are plotted in Figure 9. As shown in Figure 6 of Zhang and McMurry,¹¹ the experimental results for Fresno are bracketed by the theoretical curves for SR = 0 and SR = 1.

The effect of the ambient gas-to-particle distribution on NO_3^- volatilization is illustrated by Figure 10, which is based on monthly average RAAS filter and continuous HNO_3 measurements in Fresno. Figure 10a shows that the highest HNO_3 concentrations occurred during the warmest (and driest) months, when PNO_3^- concentrations were lowest. This follows from the dependence of the gas-particle equilibrium for NH_4NO_3 (eq 1) on temperature and RH. Figure 10b shows a strong correlation ($r = 0.93$) between the fraction of particulate NO_3^- volatilized during sampling and the ratio of ambient HNO_3 -to-total NO_3^- . The relationship is nearly 1:1, in which:

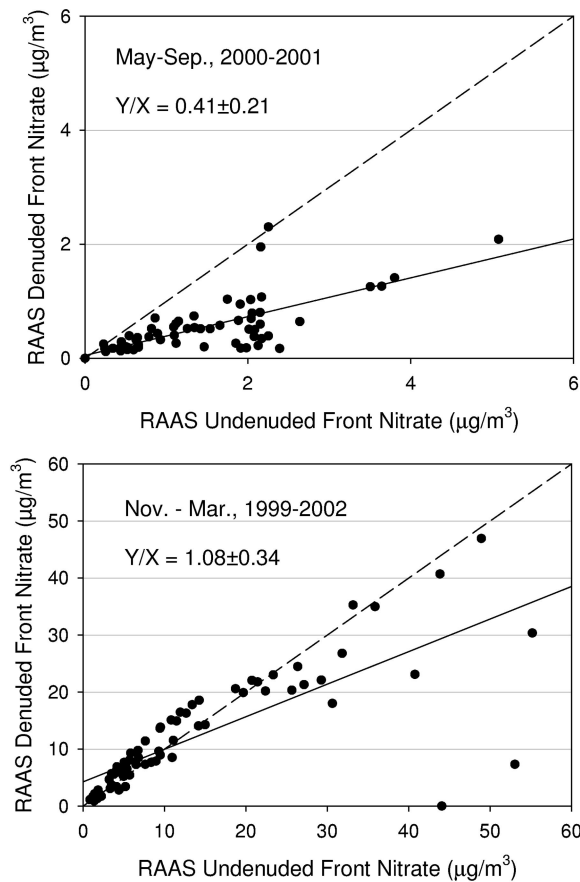


Figure 8. Comparison of daily HNO_3 -denuded and undenuded front quartz-fiber filter nonvolatilized NO_3^- from the RAAS in Fresno, CA, for: (a) warm months (May to September 2000–2001); and (b) cold months (November to March 1999–2002).

$$\text{Volatilized } \text{NO}_3^- / \text{PNO}_3^- = 1.13 (\text{HNO}_3 / [\text{HNO}_3 + \text{PNO}_3^-]) - 0.05 \quad (4)$$

For HNO_3 -denuded RAAS filter samples, volatilization of NH_4NO_3 from the front quartz-fiber filter represents the re-establishment of the NH_3 - HNO_3 equilibrium that existed in the ambient atmosphere. Equilibrium is not attained when all of the PNO_3^- evaporates.

Hering and Cass¹⁴ estimated volatilized NO_3^- for samples collected in Los Angeles using thermodynamic equilibrium constants (K) derived by Mozurkewich²² as a function of temperature (T), where:

$$\ln K = 118.87 - \frac{24084}{T} - 6.025 \ln T \quad (5)$$

Mozurkewich²² also specified additional terms to eq 5 that account for the effects of RH on K , but these were not applied by Hering and Cass.¹⁴ K defines the maximum

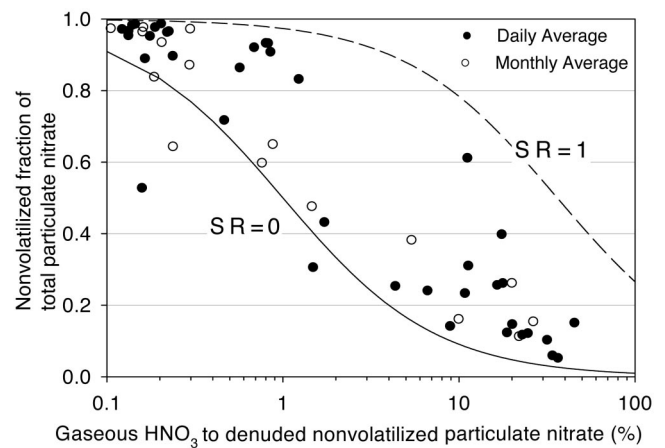


Figure 9. Particulate NO_3^- sampling efficiency for the RAAS HNO_3 -denuded front quartz-fiber filter as a function of the ratio of ambient HNO_3 to denuded front quartz-fiber filter NO_3^- concentration: solid line is the theoretical relationship for all gas phase removed (i.e., $\text{SR} = 0$); and dashed line is the theoretical relationship for gaseous NH_3 and HNO_3 at $\text{SR} = 1$. The x-axis represents the percentage of the average ambient HNO_3 concentration to the NO_3^- concentrations measured on the front quartz-fiber filter in the HNO_3 -denuded channel. The y-axis is the ratio of the nonvolatilized NO_3^- concentration on the denuded front quartz-fiber filter to total PNO_3^- (which is the sum of the denuded front quartz-fiber filter [nonvolatilized] and back-up nylon-membrane filter [volatilized] NO_3^- concentrations).

(saturation) concentrations of NH_3 and HNO_3 in equilibrium with solid- or aqueous-phase NH_4NO_3 in a system that contains only these species. Hering and Cass¹⁴ presented the following equation to convert K in units of squared nano-bars (nb^2) to volatilized NO_3^- (ΔNO_3^-) concentrations ($\mu\text{g}/\text{m}^3$):

$$\Delta\text{NO}_3^- = \frac{745.7}{T} \frac{1}{24} \sum_{i=1}^{24} \sqrt{K_{\text{amb},i}} \quad (6)$$

where $K_{\text{amb},i}$ is the equilibrium constant for the i th hour. Eq 6 assumes complete removal of NH_3 and HNO_3 before the filter and that volatilized NO_3^- approaches equilibrium with particulate NH_4NO_3 remaining on the filter. Hering and Cass¹⁴ noted that $K^{1/2}$ approximately doubles with a 5 °C increase in temperature. To account for an increase in the sample filter temperature with respect to ambient temperature, they defined κ as:

$$\kappa = \frac{\sqrt{K_{\text{filter}}}}{\sqrt{K_{\text{amb}}}} \quad (7)$$

where K_{filter} and K_{amb} are the NH_4NO_3 dissociation constants at the filter and ambient temperatures, respectively. To account for partial depletion of NH_3 and HNO_3 at equal molar concentrations before the filter, Hering and

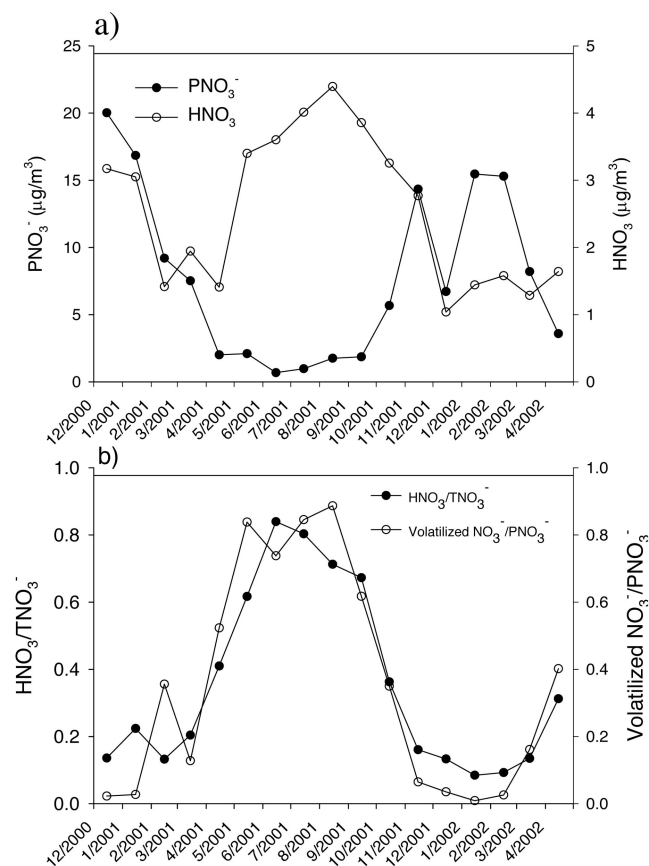


Figure 10. (a) Monthly ratio of RAAS total PNO_3^- and HNO_3 at the Fresno Supersite from December 2000 through April 2002; and (b) monthly ratio of HNO_3 to total NO_3^- (TNO_3^- , which is HNO_3 [as equivalent NO_3^-] + PNO_3^-) and monthly ratio of volatilized NO_3^- to PNO_3^- in Fresno from December 2000 through April 2002.

Cass¹⁴ defined γ as the fraction of vapor penetrating through the inlet to the filter. To account for the effects of temperature increase and removal of vapor before the filter, Hering and Cass¹⁴ expanded eq 6 as follows:

$$\Delta\text{NO}_3^- = \left[\frac{745.7}{T} \right] (\kappa - \gamma) \frac{1}{24} \sum_{i=1}^{24} \sqrt{K_{\text{amb},i}} \quad (8)$$

They applied eq 8 to data from Los Angeles and Upland, CA, with $\kappa - \gamma = 1$ and found good agreement between estimated and measured volatilized NO_3^- under the constraint that the estimated value could not exceed PNO_3^- . This constraint is necessary because eq 6 or eq 8 overestimate volatilized NO_3^- when the gas phase is completely denuded under conditions where the ambient gas concentrations are much higher than particulate NH_4NO_3 concentrations. This is illustrated in Figure 10a at the Fresno Supersite for the month of September. In this case, if all of the ambient HNO_3 was denuded and all of the particulate NH_4NO_3 on the filter evaporated, the resulting HNO_3 concentration behind the filter would be much

lower than its initial ambient concentration. Whereas the assumption that $\kappa - \gamma = 1$ can represent a range of cases of increased filter temperature and fractional penetration of NH_3 and HNO_3 gases to the filter, it reduces eq 8 to eq 6 in practice.

Because all of the HNO_3 and possibly none of the NH_3 was removed by the HNO_3 denuder in the SFS, neither eq 6 nor eq 8 strictly represents NO_3^- volatilization at the Fresno Supersite. To illustrate this, eq 6 was applied to warm (May–September) and cold (November–March) months for daily Fresno and Bakersfield SFS samples taken from December 2, 1999, through February 3, 2001. NH_4NO_3 thermodynamic equilibrium constants (K) as a function of temperature only and both temperature and RH were calculated according to eq 5 of Mozurkewich.²² As in Hering and Cass,¹⁴ daily average K were obtained from hourly average K . As expected, volatilized NO_3^- was overestimated during the warm months in every sample by an average factor of 11. Values estimated from equilibrium constants based on temperature and on temperature and RH are compared with measurements for the cold months, as shown in Figure 11, which demonstrates that volatilized NO_3^- based on K was overestimated in most cases. This is probably because of the presence of NH_3 in the sampling stream, which suppresses volatilization of NH_4NO_3 even when all of the HNO_3 has been denuded and/or to the presence of nonvolatilized NO_3^- associated with sea salt or mineral aerosols.

To account for the complete removal of HNO_3 but not of NH_3 and for the effects of heating in the sampler, the Simulating Composition of Atmospheric Particles at Equilibrium (SCAPE) thermodynamic equilibrium model of Kim et al.²³ was applied. This model describes the

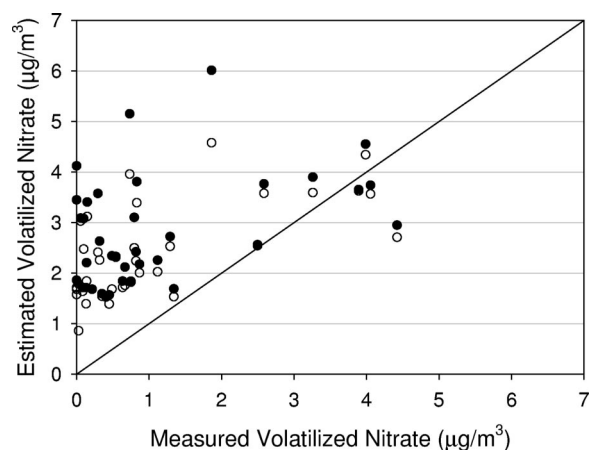


Figure 11. Comparison of volatilized NO_3^- estimated from K with volatilized NO_3^- measured with SFS at the Fresno and Bakersfield sites during the cold months (November to March). K is a function of temperature in the closed circles; K is a function of temperature and RH in the open circles.

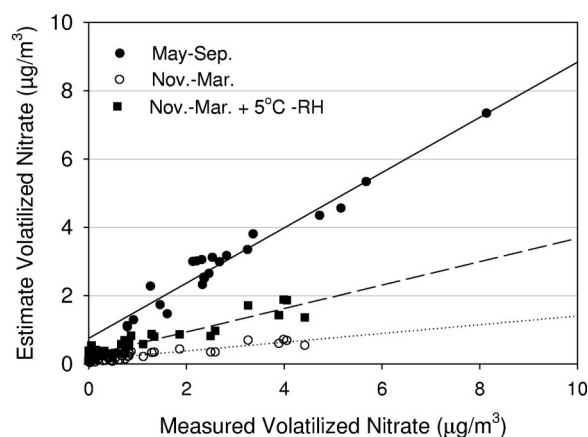


Figure 12. Measured 24-hr average volatilized NO_3^- at the Fresno and Bakersfield sites from December 2, 1999, to February 3, 2001, compared with volatilized nitrate estimated with the SCAPE model for warm months (May to September), cold months (November to March), and for the cold months with temperature raised by 5 °C and RH lowered according to the relationships shown in Figure 3 between the hours of 10:00 a.m. and 6:00 p.m. PST.

gas-particle equilibrium for complex gas and particle mixtures. The model input requires water-soluble cations and anions, such as sodium (Na^+), calcium (Ca^{2+}), magnesium (Mg^{2+}), sulfate (SO_4^{2-}), carbonate (CO_3^{2-}), total equivalent NH_3 (gaseous NH_3 plus particulate NH_4^+), total equivalent HNO_3 (gaseous HNO_3 plus particulate NO_3^-), and chloride (Cl^-) as hydrochloric acid (HCl). Total NH_3 was measured on SFS samples. Because HNO_3 was denuded, PNO_3^- is used as model input, and the model estimates the retained and volatilized NO_3^- . Ca^{2+} , Mg^{2+} , and CO_3^{2-} were not measured, and zero concentrations are assumed. Twenty-four-hour average chemical concentrations at the Fresno and Bakersfield sites were applied with corresponding hourly average temperature and RH, and the estimated equilibrium concentrations were used to calculate 24-hr averages.

Estimated and measured volatilized NO_3^- are plotted in Figure 12 for warm and cold months. The results are summarized in Table 2. During the warm months, when NO_3^- volatility is high, the agreement is good, with an

average absolute difference (AAD) of 24% and a correlation (r) of 0.95. During the cold months, however, volatilized NO_3^- was underestimated. Underestimation of volatilized NO_3^- was also seen for the 15-day winter-intensive periods. Because the winter-intensive samples captured the diurnal variation of gas and particle concentrations, underestimation of volatilized NO_3^- in the 24-hr average RAAS samples during cold months cannot be explained by such variation. Hering and Cass¹⁴ demonstrated that filter temperatures that are higher than ambient temperatures can increase NO_3^- volatilization in undenuded and denuded samples. Underestimation of NO_3^- during cold months may be related to heating of the sampler plenum during daylight hours. To test this, the model was rerun with hourly temperatures increased by 5 °C between the hours of 10:00 a.m. and 6:00 p.m. PST. The corresponding reduction in RH was estimated using the relationships between temperature and RH presented in Figure 3. As shown in Table 2, this increased the average estimated cold months volatilized NO_3^- from 0.41 to 1.21 $\mu\text{g}/\text{m}^3$ and increased the correlation between estimated and measured volatilized NO_3^- from 0.75 to 0.91.

These results suggest that the utility of thermodynamic models for estimating volatilized NO_3^- depends on the available measurements and sampling strategy. Knowledge of the ambient gas concentrations is required for eq 2 and eq 3. The use of simple thermodynamic constants is precluded unless both NH_3 and HNO_3 have been denuded from the sample air, and reactions of these gases with other species have been accounted for.²⁴ This was not the case in Fresno, where NH_3 concentrations exceeded those of total NO_3^- . NH_3 concentrations can be estimated for SFS samples as the difference between the back-up citric acid-impregnated filter NH_3 and the NH_3 equivalent of volatilized NO_3^- . Average warm- and cold-month NH_3 concentrations in Fresno were 9.3 ± 3.2 and $10.5 \pm 4.6 \mu\text{g}/\text{m}^3$, respectively. The corresponding average HNO_3 concentrations based on continuous measurements were 3.6 ± 1.7 and $2.1 \pm 1.6 \mu\text{g}/\text{m}^3$, respectively.

Table 2. Estimation of volatilized NO_3^- in SFS samples from Fresno and Bakersfield during the CRPAQS using the SCAPE thermodynamic equilibrium model.

Season	Avg. Measured Volatilized NO_3^- ($\mu\text{g}/\text{m}^3$)	Avg. Estimated Volatilized NO_3^- ($\mu\text{g}/\text{m}^3$)	Avg. Measured % Volatilization ^a	Avg. Estimated % Volatilization ^a	r^b
May-Sep.	2.4	2.5	77	84	0.95
Nov.-Mar.	1.51	0.41	22	8.3	0.75
Nov.-Mar. ^c	1.51	1.21	22	22	0.91

^a(Volatilized NO_3^- /total particulate NO_3^- [PNO_3^- , which is the sum of nonvolatilized and volatilized NO_3^- in a HNO_3 -denuded channel]) \times 100; ^bCorrelation between estimated and measured volatilized NO_3^- ; ^cAssume 5 °C heating in the sampler.

For comparison, daily average NH_3 and HNO_3 measured by denuder difference during the winter-intensive study were 9.3 ± 2.3 and $2.1 \pm 1.6 \mu\text{g}/\text{m}^3$, respectively. Detailed thermodynamic equilibrium models, such as SCAPE require total equivalent NH_3 and HNO_3 as model input, which include the retained and volatilized particulate and gas concentrations, if the gases have not been denuded. Such models also assume that the particle chemistry is internally mixed. Thus, NO_3^- volatilization may not be accurately simulated in the presence of externally mixed sodium nitrate (NaNO_3), for example. Whereas measurement of NH_3 and HNO_3 is useful in understanding the relationships between gaseous precursors and particles in the atmosphere, it is more cost-effective to measure volatilized NO_3^- directly.

Implications for $\text{PM}_{2.5}$ Standards

The state of California has drafted a proposal for a 24-hr average $\text{PM}_{2.5}$ standard of $25 \mu\text{g}/\text{m}^3$.²⁵ Hering and Cass¹⁴ and Ashbaugh and Eldred⁸ demonstrated that NO_3^- volatilization causes a negative bias for $\text{PM}_{2.5}$ mass by filter measurements. This is also the case in California's Central Valley. Figure 13 presents the daily average ratio of vola-

tilized NH_4NO_3 to actual $\text{PM}_{2.5}$ mass concentration (sum of measured $\text{PM}_{2.5}$ mass and volatilized NH_4NO_3) along with the measured $\text{PM}_{2.5}$ mass concentrations. For the 14-month period, an average of 16, 7.9, and 12.3% of the actual $\text{PM}_{2.5}$ mass was lost through volatilization at the Fresno, Angiola, and Bakersfield sites, respectively. The corresponding maximum daily losses were 44, 33, and 32% of actual 24-hr $\text{PM}_{2.5}$ mass at the three sites, respectively. The 24-hr $\text{PM}_{2.5}$ standard under consideration, $25 \mu\text{g}/\text{m}^3$, was exceeded on 14, 7, and 15 days from December 2, 1999, to February 3, 2001, at the Fresno, Angiola, and Bakersfield sites, respectively, according to measured $\text{PM}_{2.5}$. If the $\text{PM}_{2.5}$ measurement had included volatilized NH_4NO_3 , the standard would have been exceeded on an additional 2, 2, and 5 days at the Fresno, Angiola, and Bakersfield sites, respectively, over the 14-month CRPAQS period. Whereas NO_3^- evaporative losses are highest during warmer months, only two of the nine "excess" exceedances occurred during summer months (June, July, or August).

Nitrate volatilization from Teflon-membrane filters in FRM samplers is related to the ratio of ambient HNO_3 to sampled NO_3^- concentration, deposition of HNO_3 in the sampler inlet, the pressure drop across the filter, and potential heating in the sampler.^{11,14} If it is true that the inlet of the FRM sampler acts as an efficient denuder for HNO_3 , as suggested by Hering and Cass,¹⁴ losses in the FRM because of evaporation of NH_4NO_3 could be similar to those found in other HNO_3 -denuded filter-based samplers. A comparison between the SFS and FRM samplers in Fresno suggests that this is indeed the case. Figure 14a shows that the SFS (denuded) nonvolatilized front quartz-fiber filter NO_3^- concentrations ($0.52 \pm 0.26 \mu\text{g}/\text{m}^3$) were similar to the (undenuded) FRM quartz-fiber filter NO_3^- concentrations ($0.81 \pm 0.33 \mu\text{g}/\text{m}^3$) during the warm months at Fresno. Figure 14b shows that the SFS PNO_3^- concentrations, which averaged $3 \pm 1.9 \mu\text{g}/\text{m}^3$, were much higher than the corresponding FRM NO_3^- concentrations during the warm months at Fresno. These results suggest that the FRM sampler effectively removes gaseous HNO_3 from the sampling stream and that volatilization of particulate NO_3^- from the front quartz-fiber filter and, by implication, the FRM Teflon-membrane filter, should be similar to that observed in the SFS.

CONCLUSIONS

Volatilization of NH_4NO_3 during aerosol sample collection in SJV was evaluated using measurements from CRPAQS and the Fresno Supersite. Particulate NO_3^- distributions were spatially and temporally consistent in the SJV. On a seasonal basis, the amount of particulate NO_3^- lost to evaporation during sampling at the Angiola, Fresno, and Bakersfield sites ranged from 3.5 to 6.5%

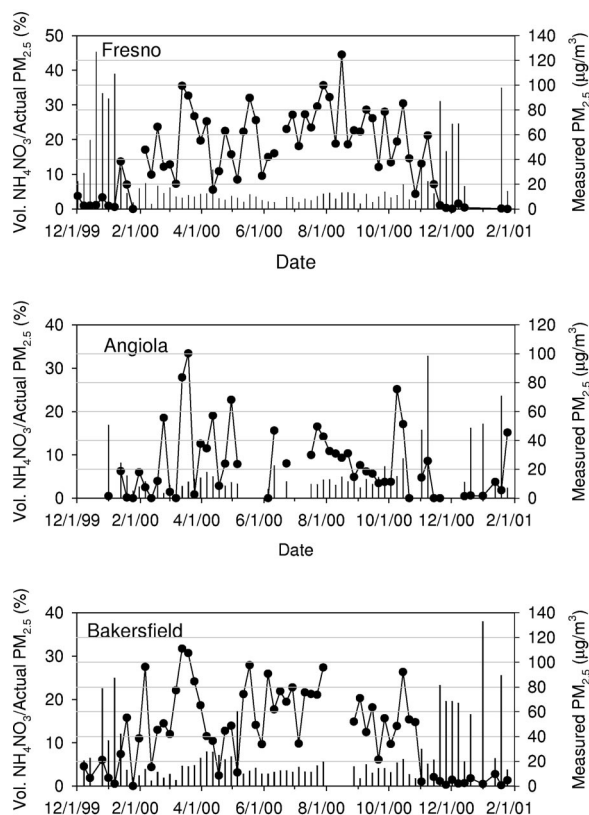


Figure 13. Daily SFS volatilized ammonium nitrate (NH_4NO_3 is $1.29 \times \text{NO}_3^-$) as a percentage of actual $\text{PM}_{2.5}$ mass (sum of measured $\text{PM}_{2.5}$ mass and volatilized NH_4NO_3) on SFS Teflon-membrane filters and measured $\text{PM}_{2.5}$ mass concentrations (vertical bars) at the Fresno, Angiola, and Bakersfield sites from December 2, 1999, to February 3, 2001.

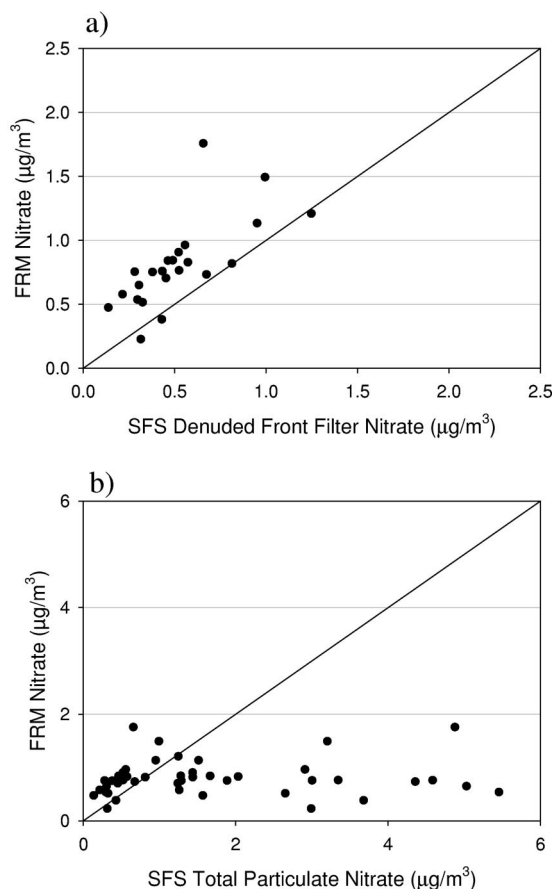


Figure 14. Comparisons between: (a) HNO_3 -denuded SFS non-volatilized front quartz-fiber filter NO_3^- and FRM quartz-fiber filter NO_3^- ; and (b) SFS total PNO_3^- and FRM quartz-fiber filter NO_3^- , during warm months (May to September, 2000) at Fresno, CA.

during cold months and from 61 to 84%, during warm months.

The degree of volatilization was correlated with annual, daily, and diurnal variations in ambient temperature, even in winter. However, the relationship between NO_3^- volatilization and temperature is indirect. Under hot and dry conditions, the equilibrium between particulate NH_4NO_3 and gaseous NH_3 and HNO_3 is shifted to the gas phase. In Fresno during summer (June–August), 80% of the total NO_3^- (the sum of gaseous HNO_3 and particulate NO_3^-) is present as HNO_3 . When HNO_3 is denuded from the sampling stream, particulate NH_4NO_3 readily evaporates to re-establish the ambient equilibrium.

Measurement of $\text{PM}_{2.5}$ mass concentration on Teflon-membrane filters was subject to significant negative bias because of evaporation of NH_4NO_3 during sampling. During CRPAQS, 8–16% of actual $\text{PM}_{2.5}$ mass (sum of measured $\text{PM}_{2.5}$ mass and volatilized NH_4NO_3) measured in HNO_3 -denuded samples by the SFS sampler was lost because of evaporation at the urban (Fresno and Bakersfield) and nonurban (Angiola) sites. Maximum

daily losses with respect to actual $\text{PM}_{2.5}$ mass occurred during spring and summer and reached 44% in Fresno. If, as these results suggest, the FRM sampler inlet efficiently removes HNO_3 during sampling, then NO_3^- volatilization must be considered when using such measurements to evaluate compliance with emerging $\text{PM}_{2.5}$ air quality standards. Such losses cannot be accurately estimated from NH_4NO_3 equilibrium constants alone. Detailed thermodynamic models, such as SCAPE, require comprehensive gas and particle measurements. The most straightforward means of correcting FRM $\text{PM}_{2.5}$ mass for NO_3^- volatilization is to measure it directly.

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